

Referee comment on “Particles’ phase state variability in the North Atlantic free troposphere during summertime determined by different atmospheric transport patterns and sources” by Cheng et al. submitted to ACP

Cheng et al. made a comprehensive investigation on the sources, chemical composition, and phase state of long-range transported free tropospheric particles based on individual particle analysis using multi-modal micro-spectroscopy techniques. This study found that most particles were in the liquid state and highlighted the importance of considering the mixing state, emission source, and transport patterns of particles when estimating particle phase state in the free troposphere. Though the findings are expected, the observation data provide valuable information constraining the physiochemical properties of aerosols in the free troposphere which is important in assessing aerosol associated climate effects. I agree with the comments of the other two referees that this manuscript can be published only after a major revision as there are too many errors in the submitted version.

**Major comments:**

1. My major concern is on the Section 3.3.2, the phase state of particles during long-range transport. The authors mainly investigated the phase state of organic particles applying the temperature and RH along the air mass transport path, and found that organic particles would likely be solid in most of the times. As the particle viscosity depends significantly on RH as pointed by the other two referees, I doubt the meaningfulness investigating the phase state at each air mass path with a wide variation in RH as shown in Fig. S10. I suggest adding a figure showing the variation of predicted viscosity with RH and T (similar to the figures in (Li and Shiraiwa 2019, Petters, Kreidenweis et al. 2019)) and investigating the phase state at free troposphere-relevant conditions. In addition, the authors applied a single value for the dry glass transition temperature, which, however, would be changed due to the change in the chemical composition during the long range transport. Finally, could the authors add some discussion that based on the inorganic component types you have observed, how you expect the phase state variation of inorganic components during the long range transport at free tropospheric RH

and  $T$ ? It would be helpful supporting the implication what you wrote in the Conclusion section that the particles in the FT probably remain liquid.

2. Mixing state plays an important role in the phase state of ambient particles; however, the authors did not mention other factors that may impact phase state significantly. Besides the influences of surface tension on aspect ratio and thus the prediction of phase state mentioned by Referee #1, the influence of particle size should be considered and discussed as well. Several studies have found that the size of particles influence the viscosity (Cheng, Su et al. 2015, Petters and Kasparoglu 2020). Did you see the difference in the phase state between the particles collected on the 3<sup>rd</sup> and 4<sup>th</sup> states of the impactor? Would the change of particle size affect the phase state during the long range transport? Secondly, the authors only mentioned the inorganic components could decrease the viscosity of internally mixed particles. They missed a recent study showing that increasing inorganic fraction can increase aerosol viscosity through cooperative ion-molecule interactions (Richards, Trobaugh et al. 2020).

**Specific comments:**

**Manuscript:**

3. I recall the comments by the other two referees that the RH in the ESEM should be clearly pointed out as the particle phase state depends significantly on RH.
4. Give the full name of “SEM” at Line 68 instead of at Line 71. Are SEM and ESEM the same?
5. Line 125. Change “Experimental” to Experiments.
6. Line 177-178. “87 for S3 and 37 for S5 for Pico 2015, and 142 and 171 particles for S3-3 and S4-2 for Pico 2017”.  
These data are not same as those in Table S2 and Table S3. Please check which are correct.
7. Line 190, I don’t understand what TCA is proportional to?
8. Line 245. Explain how you determined the air mass source is wildfire from “CO source contributions”.

9. Line 277-281, the data described for SA1, SA2 and SA3 are different from the corresponding data in Table 1.

10. Line 284-286, “and S1, S3, and S6 were influenced by both anthropogenic and wildfire CO emissions in North America (~56 %, ~79 %, ~40 %, and ~59 % for anthropogenic CO source, and ~42 %, ~19 %, ~53 %, and ~25 % for wildfire CO sources, respectively).”

Check the values (there are four values for three samples).

11. Line 289. Change “Chemical-resolved” to “Chemically-resolved”.

12. Line 292. Change “>400 particles cm<sup>-3</sup>” to “>400 particles cm<sup>-3</sup>”

13. Line 296. “Our particles are internally mixed based on tilted transmission electron microscopy (TEM, the titled angle was 70°) (Fig. S8).”, Line 328. “This observation is consistent with their STXM images and tilted TEM images (Fig. S8)”.

Give a more detailed explanation how an internal mixing state is determined?

Line 297. Change “titled angle” to “tilted angle”.

14. Line 298. “Fig. 2(b to i) show” should be Fig. 3(b to i).

15. Line 304. “area equivalence diameter” . Do you mean “area equivalent diameter”?

16. Line 306. The values of 79.6% and 1.1% did not match the values in Table S2.

17. Line 323. “Figure 4 shows the STXM-NEXAFS Carbon K-edge chemical speciation maps and spectra of four typical particle mixing states of OC (green), IN (blue), and EC (red) found in S3-3 and S4-2, which are (a) organic particle (green), (b) EC core (red) and coated by OC (green), (c) internally mixed EC (red) and In (cyan) coated by OC (green), and (d) In (cyan) coated by OC (green)”.

Do “blue” and “cyan” both indicate the inorganics? DO “IN” and “In” both indicate the inorganics? And the description here is different from the caption of Figure 4.

18. Line 331. “all samples”

Check Figure S9 is for the results of all samples of only seven samples.

**19.** Line 332. “S3-3 and S4-4 samples”

Do you actually mean S3-3 and S4-2 samples? I do not see S4-4 in Figure S9, and in Table S2, the sample analyzed by STXM-NEXAFS is sample S4-1. Also check the values that did not match the ones in Table S2.

**20.** Line 344. “Figure 5 shows violin plots of the ‘corrected’ aspect ratio (left) and representative tilted images (right) for Pico 2014 (a to c), Pico 2015 (d to i), and Pico 2017 (j to q).”

The description here is different from the caption of Fig. 5. Correct it.

**21.** Line 368. “The substantial fraction of solid and semisolid particles might be less oxidized”

In Table 1, I found that SA1 and S6, whose average aging time is both longer than 16 days, have smaller fraction of liquid particles than other samples. Can you explain why the fraction of liquid particles is smaller with longer aging time?

**22.** Line 379. Change “5(a, d, e, I, and j to o))” to “5(a, d, e, i, and j to o)”

**23.** Line 383. “For S4-2, a possible reason is that the volatile and less viscous species of particles collected on the TEM grid have already evaporated and left these tiny residuals around those big particles (see Fig. 5(f) right panel) due to difference in temperature, RH, and pressure between OMP and SEM chamber.”

Does this problem also exist in the experiments of other samples?

**24.** Line 402. I did not see the viscosity of BBOA predicted in DeRieux et al. (2018) is up to  $10^{12}$  Pa s. I suggest you only show what is the range of the viscosity under the atmospherically relevant RH. Add Li et al. (2020) who also calculated the viscosity of BBOA based on volatility distributions (Li, Day et al. 2020).

**25.** Line 416. “Shaded areas represent regions of different phase states (liquid: blue, semisolid: green, and solid: red), with the boundaries of each region based on (O’Brien et al., 2014).”

Can you give a more detailed explanation how to get the boundary lines?

**26.** Line 430. “We used the density ( $\rho_{\text{org}}$ ), hygroscopicity ( $\kappa_{\text{org}}$ ), and dry glass transition temperature ( $T_{\text{g,org},0}$ ) of organic particles as reported by Schum et al., 2018 (see SI) since we

do not have molecular compositions for our samples and Schum et al., 2018's samples were also collected at OMP during the same seasonal period (June and July).”.

The previous analysis in this manuscript mentioned that the composition of organic matter is quite different for different samples. Therefore,  $T_{g,org,0}$  would be changed. There are three samples in the study of Schum et al. (2018), and the estimated  $T_g$  are also varied. Discussion of the uncertainties in  $T_{g,org,0}$  is better added.

27. Line 441, also cite (Schmedding, Rasool et al. 2020, Li, Carlton et al. 2021).
28. Line 490, cite (Li, Carlton et al. 2021, Shrivastava, Rasool et al. 2022).
29. Line 930. Change “solid black cycles” to “solid black circles”?
30. There is no need to use italics in the columns 12 and 13 in the first row in Table 1.
31. What does the colorbar in Figure 1 indicate?
32. The inserted figures should be described in the caption of Figure 3.
33. Change “SA1” to “SA2” for panel b in Figure 5.

#### **Supporting Information:**

34. Line 2. The title in the supplementary is different from the title in the manuscript.
35. Line 21. “where  $T_{g,w}$  is equal to 136 K, is the  $T_g$  for pure water”.  
Cite (Kohl, Bachmann et al. 2005).
36. Line 29. “Moreover,  $\kappa_{GT}$ ,  $T_{g,w}$ ,  $\kappa_{org}$ , and  $\rho_{org}$  were assumed to be 2.5 (Shiraiwa et al. 2017), 309 K (Schum et al. 2018), 0.12 (Schum et al. 2018), and  $1.4 \text{ g cm}^{-3}$  (Schum et al. 2018), respectively.”  
Why 309 K is for  $T_{g,w}$ ? Check it.
37. Figure S2. What the x-axis stands for in figures b to r?
38. In Figure S2 and Figure S3, are the relative atomic ratios of elements same as the relative element weight?

39. Figure S4. Change “Jun” to “June”.
40. In Fig. S5-S6, I don’t understand why the residence time is in percentage and how did you calculate it?
41. In the caption of Figure S10, “Mean ambient temperature (blue) and the predicted RH-dependent  $T_{g,org}$  values (green)”. The ambient  $T$  is actually in green and  $T_{g,org}$  is in blue in the figure.

## References

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